State of California
Air Resources Board

Method 6

Determination of Sulfur Dioxide Emissions from Stationary Sources

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Amended: ______________

Note: this document consists of the text of the proposed amendment to Method 6. Proposed deletions are noted by graphic screen and proposed additions are noted by underline.

METHOD 6 - DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

1 Principle and Applicability

1.1 Principle

A gas sample is extracted from the sampling point in the stack. The sulfuric acid mist (including sulfur trioxide) and the sulfur dioxide (SO_2) are separated. The sulfur dioxide (SO_2) fraction is measured by the barium-thorin titration method.

1.2 Applicability

This method is applicable for the determination of sulfur dioxide (SO_2) emissions from stationary sources. The minimum detectable limit of the method has been determined to be 3.4 milligrams (mg) of SO_2/m^3 (2.12×10^{-7} lb/ft^3). Although no upper limit has been established, tests have shown that concentrations as high as 80,000 mg/m^3 of SO_2 can be collected efficiently in two midget impingers, each containing 15 milliliters of 3 percent hydrogen peroxide, at a rate of 1.0 lpmliter/min for 20 minutes. Based on theoretical calculations, the upper concentration limit in a 20-liter sample is about 93,300 mg/m^3.

Possible interferents are free ammonia, water-soluble cations, and fluorides. The cations and fluorides are removed by glass wool filters and an isopropanol bubbler, and hence do not affect the SO_2 analysis. When samples are being taken from a gas stream with high concentrations of very fine metallic fumes (such as found in inlets to control devices), a high-efficiency glass-fiber filter must be used in place of the glass wool plug (i.e., the one in the probe) to remove the cation interferents.

Free ammonia interferes by reacting with SO_2 to form particulate sulfite and by reacting with the indicator. If free ammonia is present (this can be determined by knowledge of the process and noticing white particulate matter in the probe and isopropanol bubbler), alternative methods subject to the approval of the Control Agency's Authorized RepresentativeExecutive Officer, are required.

Any modification of this method beyond those expressly permitted shall be considered a major modification subject to the approval of the Executive Officer. The term Executive Officer as used in this document shall mean the Executive Officer of the Air Resources Board (ARB), or his or her authorized representative.

2 Apparatus

2.1 Sampling

The sampling train is shown in figure 6-1, and component parts are discussed below. The tester has the option of substituting sampling equipment described in Method 8 in place of the midget impinger equipment of Method 6. However, the Method 8 train must be modified to include a heated filter between the probe and isopropanol impinger, and the operation of the sampling train and sample analysis must be at the flow rates and solution volumes defined in Method 8.

The tester also has the option of determining SO_2 simultaneously with particulate matter and moisture determinations by (1) replacing the water in a Method 5 impinger system with 3 percent peroxide solution, or (2) by replacing the Method 5 water impinger system with a Method 8 isopropanol-filter-peroxide system. The analysis for SO_2 must be consistent with the procedure inof Method 8.

2.1.1 Probe

Borosilicate glass, or stainless steel (other materials of construction may be used, subject to the approval of the AdministratorExecutive Officer), approximately 6-mm inside diameter, with a heating system to prevent water condensation and a filter (either in-stack or heated out-stack) to remove particulate matter, including sulfuric acid mist. A plug of glass wool is a satisfactory filter.

2.1.2 Bubbler and Impingers

One midget bubbler, with medium-coarse glass frit and borosilicate or quartz glass wool packed in top (see Figure 6-1) to prevent sulfuric acid mist carryover, and three 30-ml midget impingers. The bubbler and midget impingers must be connected in series with leak-free glass connectors. Silicone grease may be used if necessary to prevent leakage.

At the option of the tester, a midget impinger may be used in place of the midget bubbler.

Other collection absorbers and flow rates may be used, but are subject to the approval of the AdministratorExecutive Officer. Also, but the collection efficiency must be shown to be at least 99 percent for each test run and must be documented in the report.

If the efficiency is found to be acceptable after a series of three tests, further documentation is not required. To conduct the efficiency test, an extra absorber must be added and analyzed separately. This extra absorber must not contain more than 1 percent of the total SO_2.

2.1.3 Glass Wool

Borosilicate or quartz.

2.1.4 Stopcock Grease

Acetone-insoluble, heat-stable silicone grease may be used, if necessary.

2.l.5 Temperature Gauge

Dial thermometer, or equivalent, to measure temperature of gas leaving impinger train to within 1°C (2°F).

2.1.6 Drying Tube

Tube packed with 6- to 16-mesh indicating-type silica gel, or equivalent, to dry the gas sample and to protect the meter and pump. If the silica gel has been used previously, dry at 175° C (350° F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to approval of the Control Agency's Authorized RepresentativeExecutive Officer.

2.1.7 Valve

Needle valve, to regulate sample gas flow rate.

2.1.8 Pump

Leak-free diaphragm pump, or equivalent, to pull gas through the train. Install a small surge tank between the pump and rate meter to eliminate the pulsation effect of the diaphragm pump on the rotameter.

2.1.9 Rate Meter

Rotameter, or equivalent, capable of measuring flow rate to within 2 percent of the selected flow rate of about 1000 cc/min.

2.1.10 Volume Meter

Dry gas meter, sufficiently accurate to measure the sample volume to within 2 percent, calibrated at the selected flow rate and conditions actually encountered during sampling, and equipped with a temperature gauge (dial thermometer, or equivalent) capable of measuring temperature accurately to within 3°C (5.4°F).

2.1.11 Barometer

Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm (0.1 in.) Hg. In many cases, the barometric reading may be obtained from a nearby national weather service station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for evaluation differences between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) for 30 m (100 ft) elevation increase or vice versa for elevation decrease.

2.1.12 Vacuum Gauge and Rotameter

At least 760-mm (30-in.) Hg gauge and 0-40 cc/min rotameter, to be used for leak-check of the sampling train.

2.2 Sample Recovery

2.2.1 Wash Bottles

Polyethylene or glass, 500-ml, two.

2.2.2 Storage Bottles

Polyethylene, 100-ml, to store impinger samples (one per sample).

2.3 Analysis

2.3.1 Pipettes

Volumetric type, 5-ml, 20-ml (one per sample), and 25-ml sizes.

2.3.2 Volumetric Flasks

100-ml size (one per sample) and 1000-ml size.

2.3.3 Burettes

5- and 50-ml sizes.

2.3.4 Erlenmeyer Flasks

250-ml size (one for each sample, blank, and standard).

2.3.5 Dropping Bottle

125-ml size, to add indicator.

2.3.6 Graduated Cylinder

100-ml size.

2.3.7 Spectrophotometer

To measure absorbance at 352 nanometers.

3 REAGENTS

Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. Where such specifications are not available, use the best available grade.

3.1 Sampling

3.1.1 Water

Deionized, distilled to conform to ASTM Specification D 1193-7477, Type 3. At the option of the analyst, the $KMn0_4$ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

3.1.2 Isopropanol, 80 Percent

Mix 80 ml of isopropanol with 20 ml of deionized, distilled water.

3.1.2.1

Check each lot of isopropanol for peroxide impurities as follows: shake 10 ml of isopropanol with 10 ml of freshly prepared 10 percent potassium iodide solution. Prepare a blank by similarly treating 10 ml of distilled water. After 1 minute, read the absorbance at 352 nanometers on a spectrophotometer. If absorbance exceeds 0.1, reject alcohol for use.

3.1.2.2

Peroxides may be removed from isopropanol by redistilling or by passage through a column of activated alumina; however, reagent grade isopropanol with suitably low peroxide levels may be obtained from commercial sources. Rejection of contaminated lots may, therefore, be a more efficient procedure.

3.1.3 Hydrogen Peroxide, 3 Percent

Dilute 30 percent hydrogen peroxide 1:9 (v/v) with water (30 ml is needed per sample). Prepare fresh daily.

3.1.4 Potassium Iodide Solution, 10 Percent

Dissolve 10.0 g of KI in water, and dilute to 100 ml. Prepare when needed.

3.2 Sample Recovery

3.2.1 Water

Deionized, distilledSame as in 3.1.1.

3.2.2 Isopropanol, 80 Percent

Mix 80 ml of isopropanol with 20 ml of deionized, distilled water. Same as in 3.1.2.

3.3 Analysis

3.3.1 Water

Deionized, distilledSame as in 3.1.1.

3.3.2 Isopropanol, 100 Percent

3.3.3 Thorin Indicator

1-(o-arsonophenylazo)-2-naphthol-3,6-disulfonic acid, disodium salt, or equivalent indicator. Dissolve 0.20 g in 100 ml of deionized distilled water.

3.3.4 Barium PerchlorateStandard Solution, 0.0100 N

Dissolve 1.95 g of barium perchlorate trihydrate $[Ba(Cl0_4)_2{\bullet}3H_20]$ in 200 ml distilled water, and dilute to 1 liter with isopropanol. Alternatively, 1.22 g of $[BaCl_2{\bullet}2H_20]$ may be used instead of the perchlorate. Standardize as in Section 5.5.

3.3.5 Sulfuric Acid Standard, 0.0100 N

Purchase or standardize to ±0.0002 N against 0.0100 N Na0H which has previously been standardized against potassium acid phthalate (primary standard grade).

3.3.6 Quality Assurance Audit Samples

Sulfate samples in glass vials. Each set will consist of two vials having solutions of unknown concentrations. Only when making compliance determinations, obtain an audit sample set from the appropriate EPA regional office or from the responsible enforcement agency, or from another provider approved by the Executive Officer. (Note: The tester should notify the EPA regional office or the responsible enforcement agency at least 30 days prior to the test date to allow sufficient time for delivery.)

4 PROCEDURE

4.1 Sampling

4.1.1 Preparation of Collection Train

Measure 15 ml of 80 percent isopropanol into the midget bubbler and 15 ml of 3 percent hydrogen peroxide into each of the first two midget impingers. Leave the final midget impinger dry. Assemble the train as shown in Figure 6-1. Adjust the probe heater to a temperature sufficient to prevent water condensation. Place crushed ice and water around the impingers.

4.1.2 Leak-Check Procedure

After assembly at the test site, the sampling train must be leak-checked. A leak check after each sampling run is mandatory. A leak check prior to the sampling run is optional but strongly recommended; a leak check after the sampling run is mandatory. The leak-check procedure is as follows:

Temporarily attach a suitable (e.g., 0- to 40-cc/min) rotameter to the outlet of the dry gas meter, and place a vacuum gauge at or near the probe inlet. Plug the probe inlet, pull a vacuum of at least 250 mm Hg (10 in. Hg) Hg and note the flow rate as indicated by the rotameter. A leakage rate not in excess of 2 percent of the average sampling rate is acceptable.

NOTE: Carefully release the probe inlet plug before turning off the pump.

It is suggested (not mandatory) that the pump be leak-checked separately, either prior to or after the sampling run. If done prior to the sampling run, the pump leak-check shall precede the leak-check of the sampling train described immediately above; if done after the sampling run, the pump leak-check shall follow the train leak-check. To leak-check the pump, proceed as follows: Disconnect the drying tube from the probe-impinger assembly. Place a vacuum gauge at the inlet to either the drying tube or the pump, pull a vacuum of 250 mm Hg (10 in. Hg), plug or pinch off the outlet of the flow meter, and then turn off the pump. The vacuum should remain stable for at least 30 seconds.

Other leak-check procedures may be used, subject to the approval of the Control Agency's Authorized RepresentativeExecutive Officer. The procedure used in Method 5 is not suitable for diaphragm pumps.

4.1.3 Sample Collection

Record the initial dry gas meter reading and barometric pressure. To begin sampling, position the tip of the probe at the sampling point, connect the probe to the bubbler, and start the pump. Adjust the sample flow to a constant rate of approximately 1.0 liter/min as indicated by the rotameter. Maintain this constant rate (±10 percent) during the entire sampling run. Take readings (dry gas meter, temperatures at dry gas meter and at impinger outlet and rate meter) at least every 5 minutes. Add more ice during the run to keep the temperature of the gases leaving the last impinger at 20^{o} C (68^{o} F) or less. At the conclusion of each run, turn off the pump, remove probe from the stack, and record the final readings. Conduct a leak-check as in Section 4.1.2. (This leak-check is mandatory.) If a leak is found, void the test run or use procedures acceptable to the Control Agency's Authorized RepresentativeExecutive Officer to adjust the sample volume for the leakage. Drain the ice bath, and purge the remaining part of the train by drawing clean ambient air through the system for 15 minutes at the sampling rate.

Clean ambient air can be provided by passing air through a charcoal filter or through an extra midget impinger with 15 ml of 3 percent H_20_2. The tester may opt to use simply ambient air without purification.

4.2 Sample Recovery

Disconnect the impingers after purging. Discard the contents of the midget bubbler. Pour the contents of the midget impingers into a leak-free polyethylene bottle for shipment. Rinse the three midget impingers and the connecting tubes with water, and add the washings to the same storage container. Mark the fluid level. Seal and identify the sample container.

4.3 Sample Analysis

Note level of liquid in container, and confirm whether any sample was lost during shipment; note this on analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Control Agency's Authorized RepresentativeExecutive Officer, to correct the final results.

Transfer the contents of the storage container to a 100-ml volumetric flask, and dilute to exactly 100 ml with water. Pipette a 20-ml aliquot of this solution into a 250-ml Erlenmeyer flask, add 80 ml of 100 percent isopropanol and two to four drops of thorin indicator, and titrate to a pink endpoint using 0.0100 N barium standard solution. Repeat and average the titration volumes. Run a blank with each series of samples. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is larger.

NOTE: Protect the 0.0100 N barium standard solution from evaporation at all times.

4.4 Audit Sample Analysis

4.4.1
Concurrently analyze the two audit samples and a set of compliance samples (Section 4.3) in the same manner to evaluate the technique of the analyst and the standards preparation. (Note: It is recommended that known quality control samples be analyzed prior to the compliance and audit sample analysis to optimize the system accuracy and precision. One source of these samples is listed in Section 3.3.6.)The same analysts, analytical reagents and analytical system shall be used both for compliance samples and the EPA audit samples; if this condition is met, auditing of subsequent compliance analyses for the same enforcement agency within 30 days is not required. An audit sample set may not be used to validate different sets of compliance samples under the jurisdiction of different enforcement agencies, unless prior arrangements are made with both enforcement agencies.

4.4.2
Calculate the concentrations in mg/dscm using the specified sample volume in the audit instructions. (Note: Indication of acceptable results may be obtained immediately by reporting the audit results in mg/dscm and compliance results in total mg SO_2/sample by telephone to the responsible enforcement agency.) Include the results of both audit samples, their identification numbers, and the analyst's name with the results of the compliance determination samples in appropriate reports to the EPA regional office or the appropriate enforcement agency. Include

this information with subsequent compliance analyses for the same enforcement agency during the 30-day period.

4.4.3
The concentrations of the audit samples obtained by the analyst shall agree within 5 percent of the actual concentrations. If the 5-percent specification is not met, reanalyze the compliance samples and audit samples, and include initial and reanalysis values in the test report (see Note in Section 4.4.1).

4.4.4
Failure to meet the 5-percent specification may require retests until the audit problems are resolved. However, if the audit results do not affect the compliance or non-compliance status of the affected facility, the Executive Officer may waive the reanalysis requirement, further audits, or retests and accept the the results of the compliance test. While steps are being taken to resolve audit analysis problems, the Executive Officer may also choose to use the data to determine the compliance or non-compliance of the affected facility.

5 CALIBRATION

5.1 Metering System

5.1.1 Initial Calibration

Before its initial use in the field, first leak-check the metering system (drying tube, needle valve, pump, rotameter, and dry gas meter) as follows: Place a vacuum gauge at the inlet to the drying tube and pull a vacuum of 250 mm (10 in.) Hg; plug or pinch off the outlet of the flow meter, and then turn off the pump. The vacuum shall remain stable for at least 30 seconds. Carefully release the vacuum gauge before releasing the flow meter end.

Next, calibrate the metering system (at the sampling flow rate specified by the method) as follows: Connect an appropriately sized wet test meter (e.g., 1 liter per revolution) to the inlet of the drying tube. Make three independent calibrations runs, using at least five revolutions of the dry gas meter per run. Calculate the calibration factor, Y (wet test meter calibration volume divided by the dry gas meter volume, both volumes adjusted to the same reference temperature and pressure), for each run, and average the results. If any Y-value deviates by more than 2 percent from the average, the metering system is unacceptable for use. Otherwise, use the average as the calibration factor for subsequent test runs.

5.1.2 Post-Test Calibration Check

After each field test series, conduct a calibration check as in Section 5.1.1 above, except for the following variations: (a) the leak-check is not to be conducted, (b) three, or more revolutions of the dry gas meter may be used, and (c) only two independent runs need be made. If the calibration factor does not deviate by more than 5 percent from the initial calibration factor (determined in Section 5.1.1), then the dry gas meter volumes obtained during the test series are acceptable. If the calibration factor deviates by more than 5 percent, recalibrate the metering system as in Section 5.1.1, and for the calculations, use the calibration factor (initial or recalibration) that yields the lower gas volume for each test run.

5.2 Thermometers

Calibrate against mercury-in-glass thermometers.

5.3 Rotameter

The rotameter need not be calibrated, but should be cleaned and maintained according to the manufacturer's instruction.

5.4 Barometer

Calibrate against a mercury barometer.

5.5 Barium PerchlorateStandard Solution

Standardize the barium perchlorate or chloride solution against 25 ml of standard sulfuric acid to which 100 ml of 100 percent isopropanol has been added. Run duplicate analyses. Calculate the normality using the average of a pair of duplicate analyses where the titrations agree within 1 percent or 0.2 ml, whichever is larger.

6 CALCULATIONS

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation.

6.1 Nomenclature

C_{SO2} = Concentration of SO_2, dry basis corrected to standard conditions, mg/dscm (lb/dscf).

N = Normality of barium perchloratestandard titrant, meq./ml.

P_{bar} = Barometric pressure at the exit orifice of the dry gas meter, mm Hg (in Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

T_m = Average dry gas meter absolute temperature, °K (°R).

T_{std} = Standard absolute temperature, 293°K (528°R).

V_s $\underline{V_a}$ = Volume of sample aliquot titrated, ml.

V_m = Dry gas volume as measured by the dry gas meter, dcm (dcf).

$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm (dscf).

V_{soln} = Total volume of solution in which the SO_2 sample is contained, 100 ml.

V_t = Volume of barium perchlorate<u>standard</u> titrant used for the sample, ml (average of replicate titrations)<u>ml</u>.

V_{tb} = Volume of barium perchlorate<u>standard</u> titrant used for the blank, ml.

Y = Dry gas meter calibration factor.

32.03 = Equivalent weight of sulfur dioxide.

6.2 Dry Sample Gas Volume, Corrected to Standard Conditions

$$V_{m(std)} = V_m\ Y\ \left(\frac{T_{std}}{T_m}\right)\left(\frac{P_{bar}}{P_{std}}\right) = K_1\ Y\ \frac{V_m P_{bar}}{T_m} \qquad \text{Equation 6-1}$$

where:

K_1 = 0.3858 °K/mm Hg for metric units,
= 17.65 °R/in. Hg for English units.

6.3 SO_2 Concentration

Equation to be replaced

$$C_{SO2} = K_2\ [(V_t - V_{tb})\ N\ (V_{soln} / V_s)] / V_{m(std)} \qquad \text{Equation 6-2}$$

<u>Replacement Equation</u>

$$C_{SO2} = K_2\ [(V_t - V_{tb})\ N\ (V_{soln} / V_a)] / V_{m(std)} \qquad \text{Equation 6-2}$$

where:

K_2 = 32.03 mg/meq. for metric units,

= 7.061×10^{-5} lb/meq. for English units.

<u>6.4 Relative Error (RE) for QA Audit Samples. Percent</u>

$RE = 100\ (C_d - C_a)/C_a$

where:
Cd = determined audit sample concentration, mg/dscm.
Ca = Actual audit sample concentration, mg/dscm.

7. Alternative Procedures

7.1 Dry Gas Meter as a Calibration Standard

A dry gas meter may be used as a calibration standard for volume measurements in place of the wet test meter specified in Section 5.1, provided that it is calibrated initially and recalibrated periodically according to the procedures outlined in EPA Method 5, Section 7.1, with the following exceptions: (1) the dry gas meter is calibrated against a wet test meter having a capacity of 1 liter/rev or 3 liters/rev and having the capability of measuring volume to within 1 percent; (2) the dry gas meter is calibrated at 1 liter/min (2 cfh); and (3) the meter box of the Method 6 sampling train is calibrated at the same flow rate.

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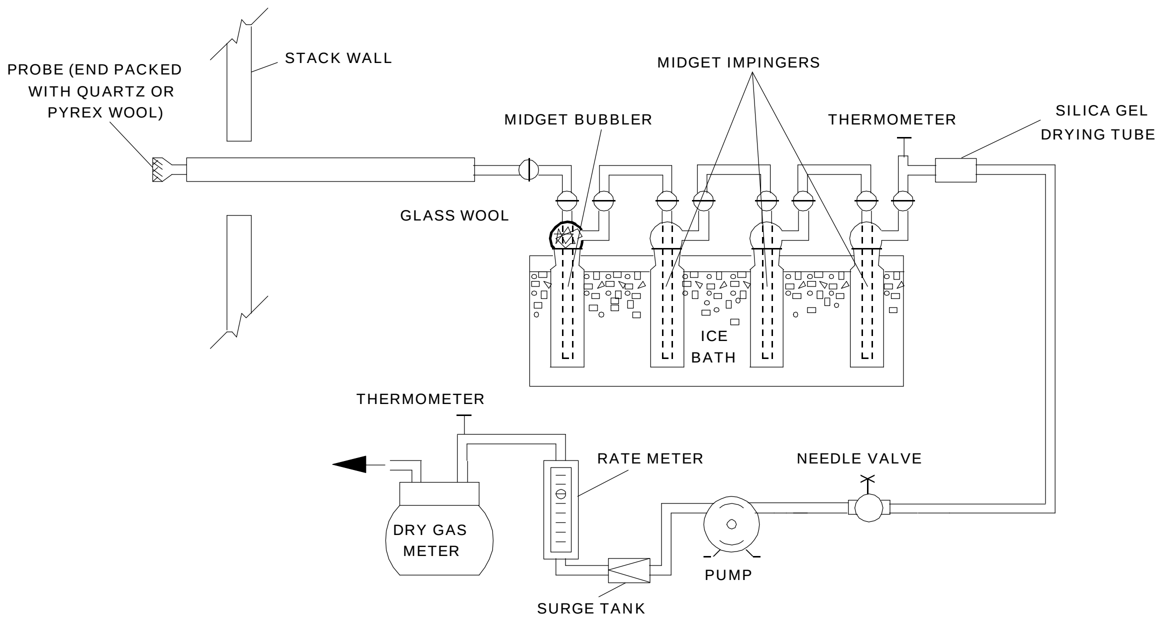

Figure 6-1. SO2 Sampling Train